

**Remarks**

The Attorney for Applicant wishes to thank Examiner Weiss for the helpful interview held on September 28, 2010, during which the references and proposed changes to the claims were discussed. Claims 1, 16, 25 and 26 are currently amended without addition of new matter. Reconsideration of the currently presented claims is respectfully requested.

***Information Disclosure Statement***

An English translation of Becker/Braun, KUNSTSTOFFHANDBUCH, Vol. 2/1, Carl Hanser Verlag, (1986), pgs. 570-595 was previously submitted on August 20, 2009 in a Supplemental Information Disclosure Statement. However, attached hereto as Appendix A is another English translation of the foreign reference for Examiner's convenience. Consideration of the Information Disclosure Statement filed 08/24/2006 is respectfully requested.

***Claim Rejections – 35 USC § 103***

In ¶11 of the last Office Action, claims 1-5, 8, and 14-18 are rejected under 35 U.S.C. 103(a) as being unpatentable over Worschech et al. (US 3,875,069) (referred to as '069) in view of Worschech et al. (4,637,887) (referred to as '887).

Worschech '069 discloses a lubricant composition comprising a mixture of (A) mixed esters of aliphatic polyols, dicarboxylic acids and long-chained aliphatic monocarboxylic acids, and (B) esters of the groups: (1) esters of dicarboxylic acids and long-chained aliphatic monofunctional alcohols, (2) esters of long-chained aliphatic monofunctional alcohols and long-chained aliphatic monocarboxylic acids, (3) complete or partial esters of aliphatic polyols and long-chained aliphatic monocarboxylic acids, in a ratio of (A) to (B) of from 1:3 to 9:1.

Worschech '069 fails to disclose a lubricant composition consisting of (a) a natural fat and/or oil with an iodine value below 10; and (b) at least one lubricant different from the natural fat and/or oil of component (a) as set forth in the currently presented claims.

Worschech '887 is directed to molding composition of polyvinyl chloride and from about 0.3 to 3% of a molding lubricant consisting essentially of triglycerides containing hydroxy fatty acid residues obtained from the hydrogenation of at least one epoxidized natural fat or oil selected from olive oil, linseed oil, sunflower oil, safflower oil, peanut oil, corn oil, palm oil, tall oil, lard oil, herring oil, whale oil, soybean oil, rapeseed oil, or tallow. Neither Worschech '069 nor Worschech '887 taken alone or in combination, teach, suggest, or disclose the currently presented claims. In light of the amendments and above arguments, Applicants respectfully request the examiner withdraw the rejection of claims 1-5, 8, and 14-18 under 35 U.S.C. 103(a) as being unpatentable over Worschech '069 in view of Worschech '887.

In ¶12 of the Office Action, claim 22 is rejected under 35 U.S.C. 103(a) as being unpatentable over Worschech et al. (US 3,875,069) (referred to as '069) in view of Worschech et al. (4,637,887) (referred to as '887) as applied to claim 1 above, and further in view of Alastalo et al. (US 2005/0009957 A1). Applicants have amended claim 16, from which claim 22 claims dependency. Applicants hereby incorporated the above arguments regarding Worschech '069 in view of Worschech '887 as presented in the remarks responsive to ¶11 of the Office Action. Alastalo et al. does not cure the deficiencies of Worschech '069 and/or Worschech '887. None of Worschech '069, Worschech '887 or Alastalo et al., alone or in combination, disclose the current invention. In light of the amendment and the above arguments, Applicants respectfully request the examiner withdraw the rejection of claim 22.

In ¶13 of the Office Action, claim 9 is rejected under 35 U.S.C. 103(a) as being unpatentable over Worschech et al. (US 3,875,069) (referred to as ‘069) in view of Worschech et al. (4,637,887) (referred to as ‘887) as applied to claim 1 above, and further in view of Haack et al. (US 5,889,102). Applicants have amended claim 1, from which claim 9 claims dependency. Applicants hereby incorporated the above arguments regarding Worschech ‘069 in view of Worschech ‘887 as presented in the remarks responsive to ¶11 of the Office Action. Haack et al. does not cure the deficiencies of Worschech ‘069 and/or Worschech ‘887. None of Worschech ‘069, Worschech ‘887 or Haack et al., alone or in combination, disclose the current invention. In light of the amendment and the above arguments, Applicants respectfully request the examiner withdraw the rejection of claim 9.

In ¶14 of the Office Action, claim 10 is rejected under 35 U.S.C. 103(a) as being unpatentable over Worschech et al. (US 3,875,069) (referred to as ‘069) in view of Worschech et al. (4,637,887) (referred to as ‘887) as applied to claim 1 above, and further in view of Dohi et al. (US 2004/0014861 A1). Applicants have amended claim 1, from which claim 10 claims dependency. Applicants hereby incorporated the above arguments regarding Worschech ‘069 in view of Worschech ‘887 as presented in the remarks responsive to ¶11 of the Office Action. Dohi et al. does not cure the deficiencies of Worschech ‘069 and/or Worschech ‘887. None of Worschech ‘069, Worschech ‘887 or Dohi et al., alone or in combination, disclose the current invention. In light of the amendment and the above arguments, Applicants respectfully request the examiner withdraw the rejection of claim 10.

In ¶15 of the Office Action, claims 7, 11-13, and 19 are rejected under 35 U.S.C. 103(a) as being unpatentable over Worschech et al. (US 3,875,069) (referred to as ‘069) in view of Worschech et al. (4,637,887) (referred to as ‘887) as applied to claims 1 and 16 above, in view of Dohi et al. (US 2004/0014861 A1) as applied to claim 10, in view of Haack et al. (US 5,889,102) as applied to claim 9 and further in view of Lindner (US 6,818,689). Applicants have amended claims 1 and 16, from which claims 7, 11-13, and 19 claim dependency. Applicants hereby incorporated the above arguments regarding Worschech ‘069 in view of Worschech ‘887 as presented in the remarks responsive to ¶11 of the Office Action. None of Dohi et al., Haack et al, or Lindner, alone or in combination, cure the deficiencies of Worschech ‘069 and/or Worschech ‘887. None of Worschech ‘069, Worschech ‘887, Dohi et al., Haack et al, or Lindner, alone or in combination, disclose the current invention. In light of the amendment and the above arguments, Applicants respectfully request the examiner withdraw the rejection of claims 7, 11-13, and 19.

***Conclusion***

In view of the amendments and remarks presented herein, Applicant submits that the present application is in condition for allowance, and such action is respectfully requested. If, however, any issues remain unresolved, the Examiner is invited to telephone Applicant's counsel at the number provided below.

Respectfully submitted,

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# APPENDIX A

English translation of Becker/Braun,  
KUNSTSTOFFHANDBUCH, Vol. 2/1,  
Carl Hanser Verlag, (1986), pgs. 570-595

Übersetzung eines Auszuges des Kunststoffhandbuchs, Vol. 2/1, Carl Hanser Verlag, (1986), pgs. 570-595

Becker/Braun, Kunststoffhandbuch, Vol. 2/1, Carl Hanser Verlag, (1986), pages 570-595

10     **6.5     Lubricants for PVC**

**Dr. Kurt Worschech, Loxstedt**

**6.5.1     Significance of the lubricant for PVC processing**

15     The use of lubricants in PVC processing has long been known; most of the product classes used industrial today were already used 20 years ago. Targeted work on researching the effect of lubricant was, however, carried out relatively late. There may be several reasons for this:

20     On the one hand, for a very long time, the processing of soft PVC masses dominated, where the use of lubricants did not play any particular role, on the other hand, the lubrication effect of lubricating substances which were present anyway was used. In the first PVC applications, the emulsifier content of the traditional emulsion polymers was a valuable processing aid. Stearic acid, which was used in  
25     the production of PVC soft cables and known from rubber processing, offered a further lubricating possibility. The lubricating effect of stabilising metal soaps

was likewise used. They therefore found their way into PVC processing early. At the end of the thirties PVC pipes free from softening agents were already prepared in Germany; montanic acid ester was already used here as lubricant. The literature remained, however, sparse, and the first publications [1,2] were first known 5 around 1960. With the extension of PVC hard processing, separation and lubrication problems appeared – the targeted used of lubricants gained increasingly in importance. Today, it can be said that the PVC processing is not only made significantly easier, but has only been enabled in the present quantities at all through addition of lubricants. Their commercial significance becomes apparent if it 10 recognised that in 1976 in Western Europe, around 40,000 t of lubricants were used for thermal plastic processing, of which more than 50 % were for the production of PVC semi-finished products and finished products. The question arises as to why PVC processing is dependent on lubricant to this extent. The reason lies in the sensitivity of this thermal plastic to thermal influences and in the high viscosity 15 of PVC melts. From this can be derived the following tasks for the lubricant.

Lubricants should be effective between the PVC particles and counteract frictional forces in mixing, plastification and deformation. In this application, on the one hand, the sensitive thermoplast and the stabilising system are protected by the 20 predominant elimination of uncontrolled frictional heat, on the other hand, the material transport and the thermoplastic deformation are made possible at relatively low temperatures, i.e. at very high viscosity of the melt. This material-protective effect (ball bearing effect) is achieved by practically every lubricant used, albeit with varying effect. Lubricants should prevent the PVC from adhering 25 to the hot steel of the conveying aggregates (screws, cylinders, rollers) or deformation equipment. They should also eliminate an adherence of the formed thermoplastic to the called metal of the calibration devices, forms and cooling rollers. These adhesion problems, which are to some extent very different, cannot be solved by every lubricant. Depending on the type of manufacture of the element,

special products are necessary. If these two most important lubrication effects are summarised, the result is that, in addition to the processing machine, this is the most important instrument for control of the processing properties of a PVC mixture. Since the lubricants not only perform actively as rheology aids, but are also –

5 since they do not disappear during the processing process – present as formulation component in the end product, care must also be taken in their selection. Certain properties of the finished PVC article can be significantly influenced by lubricants.

10 Conversely, lubricants are also used in order to provide the end product with certain properties, e.g. antiblocking or slipping effects. Such products are also rheologically effective during the processing phase and their contribution to the lubrication must be taken into account when formulating.

### 15 6.5.2 Lubrication mechanism

The discussion concerning the mode of action of lubricants in PVC, above all concerning a classification as “inner” (internal) and “outer” (external) lubricants is a central theme of many investigations regarding thermoplastic lubrication. The

20 difficulty lies firstly in definition differences and further in the lack of exact delimitations. An agreement in the area of definition appears possible. While “inner” lubricants should always import an improved flow ability of the PVC melt, the “outer” lubricants were earlier assigned exclusively the boundary phase PVC/steel as area of influence; they were classified as separating agents. However, many

25 empirical results, above all evidence concerning the compatibility [3 to 6] of different lubricants in PVC, could not be brought into line with this schematic. Significant, and supported by fundamental work, is the recognition that non-polar lubricants such as the hydrocarbon waxes are incompatible with the polar sub-

strate PVC. The compatibility increases with inclusion of polar groups in the CH<sub>2</sub> chains [2].

In new definitions [7], the area of outer lubrication has been significantly expanded and that of the inner lubrication formulated more precisely. It is a fact that significant amounts of incompatible lubricants – e.g. determined by transparency measurements – become embedded in the PVC, without the later occurrence of sweating out. These lubricants are, thus, also effective between PVC particles in the PVC associate during the processing processes and, by means of surface lubrication, facilitate transport and forming of the melts. Today, this contribution is generally considered as external lubrication. Thus, as soon as discrete lubricant phases form in the PVC associate, external lubrication also appears within the plasticised mass. External lubrication is, thus, the sum of the reduction of friction in the interphases between the individual PVC flow units and PVC/steel.

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Because of their chemical composition, external lubricants have little affinity to PVC. It should be assumed that these incompatible substances cannot penetrate into the powder grain of the PVC. After melting the lubricant, a rapid accumulation of lubricant between the individual PVC grains thus already occurs in the hot mixing operation. This highly effective coating prevents the transfer of frictional energy to the powder grain for a long time and in this way significantly lengthens the plastification time. Even after the destruction of the grain, such lubricants remain as coherent phases between the globules and are externally effective between the smaller flow units.

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The mode of action of inner lubricants can now apparently be more easily find. There is an agreement among authors that inner lubricants have a high affinity for

PVC and/or are well compatible with PVC. The term “PVC solubility” of internal lubricants has even been used [7]. Their effect is that of a “slippery plasticiser”. It is consistent with this consideration that PVC undergoes a reduction of the softening temperature by use of internal lubricants. It also explains very well the small influence of the inner lubricants on the plasticity and the possibility of higher doses. These relatively few positive aspects cannot explain however the enormous commercial significance of internal lubricants in PVC processing. Further, the evidence concerning the influence of internal lubricants guide in connection with the dispersion model of PVC melts [8, 9]. It can be imagined that lubricants with relatively small molecules, low melt viscosity and a balanced ratio of polar and non-polar groups not only externally wets PVC grain, but can also penetrate into the grain. With higher doses, the globules are also wetted. Because of the good affinity, a sufficient adhesion of the lubricant on the PVC flow units should be achieved. The formation of discrete phases of the lubricant is thus avoided even at extreme doses; saturation limits and clouding limits achieve high values.

During the important warming up and melting phases of the PVC, well compatible lubricants processes, which facilitates material transport, without disturbing the plastification. External lubricants have the opposite effect here: They favour the lubrication of larger particle associates and thus hinder the thermal homogenisation of the PVC mass. This differentiation also makes clear that the disadvantageous of purely external lubrication are accepted if formulation price and achievement of higher heat resistants of the PVC finished articles are concerned, but that the advantageous of internal lubrication are not surrendered, if it is desired to achieve optimal properties with relation to transparency surface construction and flow properties.

More difficult than a correct definition of external and internal lubricant effectiveness is a precised classification of the industrially used products within this classification. Only very particular lubricants can be classified in the described effect schematic as purely internal or purely external. It can be taken as a criterion for 5 internal effect that a lubricant only has little influence on the plastification process and does not effect any clouding of the PVC article, even in high doses. We talk of external effect when a retardation of the plastification time occurs, even at very low doses. A large group of lubricants is not conforming to this classification; for these, there is no absolute classification which is valid at every dose. Products 10 which are included in this group are compatible at lower doses and form no external lubricant phases. However, already at middling doses they reach a borderline value for compatibility. Beyond here, important retardation of the plastification time occurs and one can also observe other characteristics typical of external lubricants, such as clouding. Often, therefore, additional parameters such as dosage 15 as well as type and amount of further formulation partners decide whether a lubricant is effective internally, internally/externally or predominantly externally.

It is astonishing that according to these classification criteria, products which are known in practise as particularly effective separating agents cannot be classified 20 as purely external lubricants. Rather, they take an intermediate position. Obviously, questions of the arrangement of polar centres and the molecular size of the lubricant play an important role here.

More recent investigations indicate that with compatibility investigations and 25 transparency measurements only approximate values can be obtained, which do not always satisfactorily explain the transition from internal to external lubrication. In this connection, considerations concerning the PVC structure play a significant role, and certain variations in the lubricant behaviour can only be under-

stood by means of the finding concerning the particle flow process during PVC processing [10 to 13].

According to these views, on incorporation of internal lubricants into the PVC 5 associate, an irreversible solution of the lubricant in the PVC grain does not occur, but rather secondary bonds of the lubricant at the surface of super molecular units (globules) [9]. The bond strength is dependent on polarity, molecule size and structure of the lubricant and is probably also influenced by further formulation partners. Contrary to the molecular theory, which supposes fixed solubility limits, 10 in the globular theory, the compatibility limits are significantly influenced by processing parameters, e.g. by temperature, pressure and shear load. The bond strength is altered by such influences and accordingly the compatibility limit can also be shifted.

15 Lubricants are also already rheologically active before the plastification process, e.g. in the dry blend processing or in the first sections of the plastification aggregate. Such a powder lubrication can be very well demonstrated with rheological instruments such as plastographs. The plastification times measured at low need- 20 ing chamber temperatures (110 to 130°C) show a strong dependence on dose and on chemical composition; physical properties, such as melting point and melting viscosity also play a role [14]. The picture of values obtained shifts significantly within increasing temperature, so that, in the area of "powder lubrication", one must still be cautious with precised statements for the processing in practice.

### 6.5.3 Molecular structure and mode of action of lubricants

All PVC lubricants common in practice – with the exception of high molecular processing aids – have one thing in common: A hydrocarbon chain with a length of at least 12 C-atoms. Chain length and the number of chains are important influencing parameters. Effect and compatibility of lubricants are further dependent on the type and number of polar groups, on the structure and seize of the molecule. Generally valid evidence is obtained if rheological measurements are carried out by determination of plastograph data using simply constructed lubricants [15 to 18].

#### 6.5.3.1 Lubricants with one polar group

In a given uniform lubricant model, the compatibility decreases with increasing length of the hydrocarbon chain, the lubricant effectiveness, however, increases. This behaviour can be particularly well studied using the model of fatty alcohols. As table 6.4 shows, the increase in external lubrication effect can best be seen in the extension of the plastification time. The values concerning maxima and minima of the torque curve also often give unambiguous information concerning the lubricant behaviour (see page 589 (31) concerning a valuation of plastograph curves). All tabled data in this chapter were determined with the Plasticorder PLV 151 (Manufacturer: Brabender). The chamber temperature was uniformly 165 °C.

Table 6.4. plastograph data, measurement of fatty alcohols with varying chain length  
(rotational frequency: 30 min<sup>-1</sup>, sample weight: 29 g)

Lubricant	Plastification time [min]	Torque	
		Maximum [Nm]	15 min after Maximum [Nm]
C <sub>16-18</sub> alcohol	4.6	3.59	2.56
C <sub>22</sub> alcohol	7.3	3.25	2.51

Test composition: 100 parts by weight S-PVC, K-value 58  
5 2.0 parts by weight tribasic lead sulphate  
0.3 parts by weight calcium stearate  
2.0 parts by weight lubricant.

The above rule is not only valid for lubricants with terminal polar groups, but also  
10 for compounds in which a polar group is incorporated within the C chain. The model of linear saturated fatty acid ester is known. This class of compounds extends from butyl stearate to stearyl stearate and to even longer compounds. An ester function serves as compatibility-imparting group. It can clearly be seen from table 6.5 that the lubricant effect and accordingly the retardation of the plastification increases with increasing chain length of the esters; the maximum resistance  
15 to needing at the plastification point, on the other hand, is clearly reduced.

Table 6.5. Plastograph data, measured on wax esters with varying chain length (rotation frequency: 40 min<sup>-1</sup>, sample weight: 32 g)

C chain length of the wax ester	Plastification time [min]	Maximum torque [Nm]
32	2.0	3.54
35	8.7	2.63
39	17.8	2.20

Within certain limits, the position of a polar group within a lubricant model defined C chain length place no particular role. Thus, wax esters with one ester function and the same C chain length, but different structure, have generally comparable effect [18]. The two wax esters lauryl stearate and stearyl laurate are, e.g. not only identical in the C chain length, but also in the effect.

#### 6.5.3.2 Lubricants with *several* polar groups

With lubricants with uniform C chain length, the compatibility increases with the increase in polar groups in molecule. This rule has its limits; it can, however, be fully applied with the industrially used products today. Various triglycerides can serve as example: The compatibility increases on transition from soya oil to epoxidised soya oil and from glycerine tristearate to glycerine tri-12-hydroxystearate (table 6.6, 6.7).

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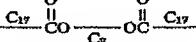
Table 6.6. Plastograph data, measured for glycerine triesters with uniform chain length but different polarities (rotation frequency: 40 min<sup>-1</sup>, sample weight: 32 g).

Lubricant	Plastification time [min]	Maximum torque [Nm]
Glycerin tri-12-hydroxystearate	19.0	2.3
Glycerin tristearate	1.2	4.8

Table 6.7. Plastograph data, measured for glycerine tri ester with uniform chain length, but varying polarity (rotation frequency: 20 min<sup>-1</sup>, sample weight: 29 g)

Lubricant	Plastification time [min]	Maximum torque [Nm]
Soya oil	11.7	3.3
Epoxidised soya oil	2.2	3.8

Table 6.8. Plastograph data, measured for diol fatty acid esters

Lubricant	Formular, schematic	Dropping point [°C]			
I ethylene glycol distearate		73.7			
II 1,6-hexane diol dipalmitate		56			
III 1,10-decane diol dimyristate		54.5			
Measurement 1 (rotation frequency: 30 min <sup>-1</sup> , sample weight: 31 g)		Measurement 2 (rotation frequency: 20 min <sup>-1</sup> , sample weight: 29 g)			
Lubricant	Plastification time [min]	Maximum torque [Nm]	Lubricant	Plastification time [min]	Maximum torque [Nm]
I	1.5	4.21	I	7.7	3.02
II	1.2	4.47	II	5.5	3.14
III	1.0	4.64	III	5.1	3.24

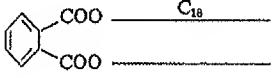
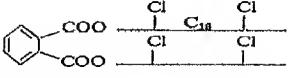
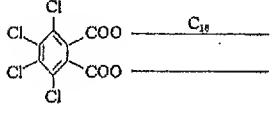
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The rule derived above with the example of the wax esters, that the effect of a lubricant with internal polar groups is relatively independent of their exact position, can no longer be fully applied if one compares lubricants with the same summary chain length but with several polar groups in different position in the

molecule. A maximum compatibility is observed if the polar groups are distributed as evenly as possible, so that relatively short C partial chains arise. The highest lubrication effect is achieved if polar and non-polar molecule portions are separated and localised. The compatibility of such lubricants is obviously decreased by the very long non-polar C chain portion (table 6.8).

The compatibility of lubricants can be decreased not only by extending the C chains (increase of the hydrocarbon part). A similar effect can also be achieved by means of an increased concentration of polar groups above a compatibility maximum. This concerns quasi "over-polar" compounds, which also turn out to be incompatible. The gain in real lubrication effect is, however, relatively modest. Table 6.9 shows that a significantly more compatible substance II arises by introduction of four Cl atoms into the lubricant model I. If, however, all polar groups are localised at the benzene core (substance III), an "over-polar" centre appears to arise, which weakens the compatibility and increases the lubrication effect.

Table 6.9. Plastograph data, measured for long chain dicarbonacideesters (rotation frequency: 20 min<sup>-1</sup>, sample weight: 29 g)

Lubricant (schematic formula)	Plastification [min]	Maximum torque [Nm]
<b>I</b> 	3.3	3.8
<b>II</b> 	1.3	4.8
<b>III</b> 	5.6	3.57

### 6.5.3.3 Lubricants with unsaturated or branched C chains

If saturated and unsaturated lubricants with the same structure are investigated, it can be clearly seen that the saturated compounds have a stronger lubrication effect  
5 and that the unsaturated parallel products are significantly more compatible. The differences are astonishingly large and can be demonstrated both with plastograph measurements (table 6.10) as well as by means of transparency investigations on PVC hard plates. Lubricants with isomeric C chains can be classified much less clearly. There are examples of a higher effectiveness of the n-chain compounds,  
10 but there are also measurements with contradictory findings. The type of branching place as much of a role as the stabiliser system or the presents of plasticiser.

Table 6.10. Plastograph data, measured on saturated and unsaturated fatty acid esters (rotation frequency:  $20 \text{ min}^{-1}$ , sample weight: 29 g)

Lubricant	Plastification time [min]	Maximum torque [Nm]	15 min after Maximum [Nm]
n-octyl stearate	6.3	13.6	12.2
n-octyl oleate	3.9	15.0	12.5
without lubricant	2.2	19.0	14.7

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### 6.5.3.4 Influence of the dosage

The influence of polar groups, as described in the above chapters, can be measured only at a certain dosage. In the range 0.5 to 2.0 phr good differentiations can  
20 be determined. The lower the selected dosage of the lubricant, the weaker the value of the information. With extreme ratios (dosage 0.2 phr) there are scarcely differences which can be determined using a plastograph or other rheological instruments. It is above all the simple fat chemical compounds, i.e. low molecular

lubricants, which show almost identical lubrication effects in this dosing range, but also pure hydrocarbons of comparable chain length, such as octadecane, make no contribution to external lubrication. Only higher molecular products, such as Fischer-Tropsch-Paraffines and HDPE-waxes show significant effect. These lubricants are distinguished from the bulk of all common types, even when used in small amounts: At 0.2 phr they already show a significant influence on plastification time and kneading resistance and thus show themselves to be strong external lubricants. In Agreement with this, synthesis paraffines also cloud at lower dosage, i.e. discrete phases form in the PVC associate.

10

In table 6.11, measurement results are shown which were determined for the number of fat chemical model substances at different doses, using the plastograph. For comparison, some lubricants were included in the test array, which come from a different raw material basis. A tin-stabilised basis mixture was used under the following test conditions: Chamber temperature: 150 °C, rotation frequency: 20 min<sup>-1</sup>, sample weight: 29 g. A dosage limit, which allows a first differentiation of the low molecular lubricants, lies around 0.5 phr. While a whole block of well compatible fat chemical substances, such as fatty alcohols, partial glycerides, hydrated castor oil and dicarboxylic acid esters shows a very uniform behaviour, a whole array of products, such as stearic acid, stearic acid anhydrid, distearylester and bis-stearoyl ethylene diamine show deviating behaviour: They are conspicuous by a significantly increased lubrication effect. In the case of the free fatty acids, such an effect can only be explained by formation of double molecules [19].

25 A conclusive fine differentiation of the internal block is only possible with a dosage of about 1 phr. It also becomes clear here that measurement parameters such as retardation of the plastification points and influence on the torque curve do not always run parallel. Lubricants with similar influence on the plastification can have completely different lubrication effect in the PVC melt. In application

phases, in which the efficiency of the lubrication represents the only selection criterion, a comparison of several suitable lubricants at a dosage of 1.0 phr provides an excellent aid to decision.

5    Rheological measurements at dosages above 2.0 phr were hardly drawn upon for the purpose of classification of the lubricants. Here, other methods, e.g. transparency measurements, play an important role, in particular, if the determination of compatibility limits is concerned. Furthermore, these limits can also be determined rheologically [9]. High doses of lubricant can be interesting for particular

10    application cases; it can be seen here that conclusions obtained at lower doses cannot simply be extrapolated to higher amounts. This is particular the case, if further substances apart from PVC and stabiliser are comprised in the system, e.g. emulsifiers. An example of this: The production of thermally tempered hard films from emulsion PVC requires lubricant doses around 4 phr [20]. Montan waxes are

15    well compatible under these formulation conditions up to 6 phr. A simple wax ester of the type cetylstearate (C chain length 34) is, at 2 phr, more compatible with lower lubrication effect compared to montanic acid ester. At 4 phr, however, it has exceeded the compatibility limit and at 6 phr shows strong over-lubrication phenomena. At high doses, we thus observe a reversal of the compatibility ratios

20    [18]. Table 6.12 shows a compilation of measurement results, which were obtained on a roller mill. The resulting sheet thicknesses and a pressure in the cap between the rolls were measured (roller mill: laboratory roller mill 450 mm x 220 mm, Manufacturer: Berstorff, temperature: 180 °C, rotation frequency: 12.5 min<sup>-1</sup>, basis formulation: 100 weight parts E-PVC, K-value 78, 0.5 weight

25    parts diphenyl thiourea).

Table 6.11. Plastograph data, measured fore different lubricants at different doses

Lubricant Model substances	Dose of the lubricant					
	0.2 phr		0.5 phr		1.0 phr	
	t [min]	M <sub>max</sub> [Nm]	t [min]	M <sub>max</sub> [Nm]	t [min]	M <sub>max</sub> [Nm]
n-octadecan	1.3	5.05	1.8	4.55	-	-
Stearic acid chloride	1.0	5.38	1.6	4.71	-	-
Stearic acid amide	1.6	5.06	2.9	4.40	-	-
Stearic acid	1.8	4.71	10.5	3.76	-	-
Stearic acid anhydride	1.8	4.97	7.5	3.81	-	-
HDPE-wax	2.9	4.20	9.1	3.50	-	-
Hydrated castor oil	1.1	5.46	1.6	4.98	-	-
Fischer-Tropsch-Parrafin	3.4	4.21	7.2	3.55	-	-
LDPE-wax	1.2	5.15	2.4	4.47	-	-
Ethylenediamine disterate	2.0	4.88	6.6	4.07	-	-
Cetyl/stearyl alcohol	-	-	1.7	4.92	-	-
1-chlor octadecane	-	-	1.2	4.98	2.1	4.33
Distearyl phthalate	-	-	1.5	5.08	2.8	3.7
Glycerine monooleate	-	-	1.8	4.60	2.0	4.40
Cetylpalmitate	-	-	2.0	4.75	3.6	3.90
Dioctadecyl ether	-	-	6.3	3.67	20.9	3.02
Distearyl ketone	-	-	1.8	4.84	4.5	3.94
Montanic acid ester	-	-	5.5	3.85	not plasticised	
without lubricant	0.8	5.52	-	-	-	-

Table 6.12. Influence of different lubricants, measured on the roller mill

Formulation	Film thicknesses [mm]	Disjoining pressure [t]
Basis formulation (B)	0.6	3.62
B + 2 phr montan wax	0.5	3.23
B + 4 phr montan wax	0.49	2.70
B + 6 phr montan wax	0.42	1.90
B + 2 phr wax ester (C <sub>34</sub> )	0.58	3.33
B + 4 phr wax ester (C <sub>34</sub> )	0.43	2.13
B + 6 phr wax ester (C <sub>34</sub> )	0.30	1.27

Table 6.13. Material examples of technically used lubricants (arranged according to effect and compatibility)

Technically used lubricant	Dropping point (TP) Melting point (SP) Solidification point (STP) [°C]	Range of effect (compatibility)
i-butyl stearate	ca 19 (STP)	Internal (highly compatible)
Distearyl phthalate	42 to 46 (TP)	
Cetyl/stearyl alcohol	48 to 54 (TP)	
Hydrated castor oil	85 to 90 (TP)	
Glyceryl monoricinoleate	> -10 (STP)	
Glyceryl monooleate	> 4 (STP)	
Glyceryl monostearate	54 to 58 (TP)	
Calcium stearate	> 140 (SP)	Internal/external (limited compatibility)
Cetyl palmitate	49 to 53 (TP)	
Steryl stearate	52 to 56 (TP)	
Partially saponified montan wax	100 to 105 (TP)	
Fatty acid complex ester	54 to 56 (TP)	
Montanic acid ester	76 to 81 (TP)	
Paraffin oil	ca. -25 (STP)	
Natural paraffines	52 to 80 (TP)	External (incompatible)
Amid wax	139 to 144 (SP)	
Oxidised PE-waxes	100 to 115 (TP)	
12-hydroxystearic acid	72 to 78 (TP)	
Stearic acid	52 to 60 (TP)	
PE-waxes	100 to 130 (TP)	
Synthetic paraffines	100 to 112 (SP)	
Heavy metal stearates	> 100 (SP)	

In connection with the previous basis measurements, table 6.13 provides a tabular overview of the most important practically used PVC lubricants according to their classification into the internal and external effect range. Plastograph measurements on tin stabilised S-PVC-mixtures with a lubricant dose between 0.2 and 5 1.5 phr were taken as basis; measurements of other authors, who sometimes work with other testing devices, were also included [9]. It should be observed that the conclusion concerning the "internal block" are still be most precised. In the transition block, the table position is already strongly dependent on the concentration of 10 the lubricant, on the stabilisation and on further formulation partners. This is also true for the "external block". In particular, the position of the free fatty acid is dependent on the stabiliser. If, in conjunction with tin stabilisers, they are considered as moderately effective lubricants, in conjunction with basic lead salts they become highly effective through formation of lead stearates. Also, in addition to 15 metal soaps, long chain fatty acids are strong external lubricants. Here, displacement and/or dilution effect might play a significant role. The transitions between the blocks are blurred; in particular between the second and third block the difference lie to a large extent more in the better compatibility of the ester waxes at higher dosage than in reduced efficiency compared to natural paraffines and amid 20 waxes (table 6.13).

#### **6.5.3.5 Separating agents**

According to the above described classifications, outer lubrication occurs not only 25 at the interfaces steal/thermoplast. In the preparation and forming of PVC, however, additives are often necessary which effect a special separation effect in these phases. All known effective separating agents are listed in a table 6.13. They are, however, astonishingly in no way identical with the strongest external lubricants.

Goods separating agents are

- metal soaps,
- montan waxes,
- fatty acid complex esters,
- 5 - oxidised long chain hydrocarbons,
- PE waxes.

The order is arbitrary. A classification is not necessary, since each of the product classes mentioned is used for special tasks. The selection depends on the process,  
10 stabilisation and requirements made on the end product. With the exception of the metal soaps, which in any case occupy a special position among lubricants, all good separating agents have relatively high molecular weight. For calander processing, the presence of polar groups in the molecule is also necessary. In this way, the lubricant gains a certain affinity to PVC and the formation of a separation  
15 layer, which would impair the necessary adhesion of the film to the roller, is avoided. For this reason; PE-waxes and low polarity oxidised long chain hydrocarbons are hardly used, or only in low doses, in calander processes.

#### 6.5.3.6 Lubricant combinations

20 In most application cases of PVC processing, several lubricants are used per formulation. The combination often arises from practical requirements: If a process requires separation effect and excellent mass flow, the classical lubricant solution is the combination fatty acid partial glyceride plus montan wax. If good tack-free  
25 property and strong external effect are required, combinations of metal soaps and fatty acids or paraffins are used. Often, such a mixture is completed by addition wax esters or dicarboxylic acid esters. Combinations of internal lubricants have not gained any practical application, on the other hand, external lubricants are very often combined. A better compatibility and higher degree of effectiveness is

expected therefrom. A type of synergy has even been claimed for certain combinations [3]. It is uncontested that several lubricants in PVC have an influence on each other and, at higher dosage amounts, also displace each other. In this way, increased effectiveness can be achieved, which can facilitate savings with suitable  
5 combinations.

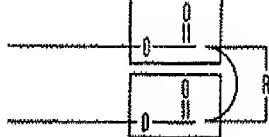
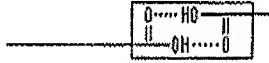
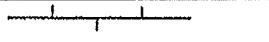
#### **6.5.4 Lubricant types and their practical application**

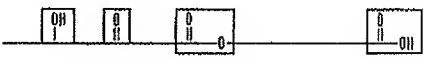
##### **6.5.4.1 Product classes and raw material basis**

10 All lubricants used in practise are derived from natural raw materials, partly by direct parts from animal or plant fats and oils, partly by synthesis from petro-chemical building blocks. Table 6.14 shows a compilation of practically all technically used lubricant types; it can, however, only take into account the most important material examples. The arrangement has been made according to raw material  
15 considerations, not according to application. Most of the listed lubricants comply with physiological standards and are widely authorised in many countries [7, 21].

Table 6.14. Technically used lubricants

Lubricant type	Chemical description / Material example	Chemical structure, schematic
Fatty acids	Palmitic / Stearic acid 12-Hydroxystearic acid	
Fatty acid esters	n-Butyl stearate i-Tridecyl stearate Glyceryl monooleate Glyceryl tri-12-hydroxy stearate (hydrated caster oil)	
Higher molecular esters from polyols, dicarboxylic acids and fatty acids ("complex esters"), also partially saponified	Ester from pentaerythritol, adipic acid and stearic acid (Ca-containing)	
Fatty alcohols	Cetyl/stearyl alcohol	
Wax esters	Cetyl palmitate, stearyl stearate	

Fatty alcohol esters	Distearyl phthalate	
	Distearyl adipate	
	Ethylenediamine distearate	
	Ca-, Zn-, Pb-stearate, Ba-, Ca-laurate	
Amide waxes	Montanic acid (C <sub>26</sub> to C <sub>32</sub> )	
	Esters from montanic acid and ethyleneglycol or butanediol	
	Montan wax, partially saponified	
<u>Hydrocarbon waxes</u>	Paraffin oil	
	Paraffin, solid, dropping point 52 to 75 °C	
	Fischer-Tropsch wax	
	LDPE-wax $\bar{M} = 2000$	
PE-waxes	HDPE-wax $M = 3000$ to 9000	

	Oxidised paraffines and oxidised PE-waxes, also partially saponified	
--	--	--

Remark: In the column "Chemical structure schematic", non-polar, long C chains are represented with a long line, polar groups with a box.

The order corresponds to the market significance. Thus, the bulk of all lubricants used is derived from fat chemistry, particularly from fatty acids; a further important group is esters and soaps of montanic acid, and as third group are listed the hydrocarbon compounds and their derivatives.

#### 10 6.5.4.2 Fields of application of fat chemical lubricants

##### Fatty acids

Technical stearic acids are used as inexpensive external lubricants in many extrusion processes for production of pipes and profiles, almost exclusively in conjunction with lead stabilisers. A particular case is the use of 12-hydroxystearic acid for the production of Ba/Cd-stabilised hard profiles. In PVC soft processing, free fatty acids are likewise often used for lubrication, also in calander processes.

##### 20 Fatty acid esters

Among these lubricants are first the alkyl stearates, consistently liquid products, which are used predominantly in semi hard and soft PVC mixtures, but also in acetate containing PVC hard masses. Polyolesters of unsaturated fatty acids have considerably greater significance. Principally the partial glyceride are widely used

internal lubricants; they are almost always used with tin stabilisers. A large amount of the calendered and extruded packaging films from PVC hard comprises glycerol oleates. Because of their excellent compatibility, they are also well suitable for use in soft processing (profiles, hoses, injection moulded parts). Partial 5 glycerides, in particular ricinoleate and 12-hydroxystearates, improve the long-term stability of PVC pieces which are stabilised with tin thioglycolates, are regarded as synergistically effective [22]. Together with sulfur-free tin compounds, a reverse effect can occur; also together with lead stabilisers, partial glycerides should not be used in light pigmented PVC mixtures, since greying appearance 10 can occur under the influence of light [23].

As an example for the support of a stabiliser system by polyol partial esters, table 6.15 can be considered. It must first be made sure that these are real synergistic effects, for this reason, rheological influences must be eliminated. It is thus 15 advisable that parallel to the stability measurements, rheological investigations are also carried out. As reference substances, are used lubricants which perform comparable on a plastograph to the test substance (table 6.16). Products which significantly strengthen the stability of PVC piece with comparable lubricant properties have synergistic effectiveness.

20 It can be seen from table 6.15 that glyceryl monostearate together with tin-thioglykolates inambiguously assists stability. Rheologically equivalent, and even superior products such as cetylstearate do not have this effect.

Table 6.15. Determination of the thermal stability (drying cupboard) (roller temperature: 170 °C, drying cupboard temperature: 180 °C

Lubricant	Dose [phr]	Stability time [min]
Without <sup>1)</sup>	0	105
Glyceryl monostearate	1.5	120
Distearyl phthalate	1.5	105
cetyl stearate	1.5	105

<sup>1)</sup>Test formulation: 100 weight parts S-PVC, K-value 58

1.5 weight parts alkyltinthioglycolate

5

The inexpensive glyceryl monostearate has lost a lot of its early significance and has been replaced in glass-clear PVC packing either by liquid partial glycerides or by the much more compatible glycerol esters of 12-hydroxystearic acid.

10 Table 6.16. Determination of the plastification time (temperature: 165 °C, rotation frequency: 40 min<sup>-1</sup>, sample weight: 32 g)

Lubricant	Dose [phr]	Plastification time [min]
Without <sup>1)</sup>	0	0.2
Glyceryl monostearate	2.0	1.2
Distearyl phthalate	2.0	1.1
cetyl palmitate	2.0	3.1

<sup>1)</sup>Test formulation: 100 weight parts S-PVC, K-value 58

1.5 weight parts alkyltinthioglycolate

0.3 weight parts calcium stearate

15

### **Fatty acid complex esters**

Solid and liquid high molecular esters based on dicarboxylic acids, polyols and long chain fatty acids (stearic acid, oleic acid, behenic acid) belong to the most 5 recent lubricant generation and are preferably used as separating agent in calander processes [24]. Partially saponified products of this class have been introduced together with Ca/Zn stabilisers likewise in the production of bottles and films; the liquid complex esters are regarded as valuable separating agents in paste processing, but also in the thermal plastic forming of PVC soft. All products of this class 10 have a number of polar groups, principally ester functions, which result in a good affinity for PVC. Even at relatively high doses (0.6 to 0.8 phr) such complex esters can be used in the production of glassclear PVC articles.

### **Fatty alcohols**

15 The mixture cetyl/stearyl alcohol is a cheap internal lubricant in PVC hard processing. The main area of use was early the production of packaging films, bottles and fittings. Because of the relatively high volatility at the constantly increasing processing temperatures, the fatty alcohols were largely substituted by better 20 suited ester lubricants. It is a particularity of the fatty alcohols that they often contribute to a marked improvement of the starting colour of PVC products. Solvent and dispersing properties of the fatty alcohols possible play a role here in the melts, which lead to a better distribution of the stabilisers.

### **25 Wax esters**

Among the ester lubricants, long chain waxes are preferred additives for the production of profiles, injection moulded articles and covered calander films from PVC hard. Lubricants of this type are particularly thermal stable and resistant

against ester splitting. They are, therefore, also suitable for outside use. Wax esters are chemically neutral and have low volatility. Although they have no synergistic properties, they are, however, compatible with all stabiliser systems. The rheological range of this material class is considerable: It extends from liquid, 5 plasticiser-compatible i-tridecylstearate to powerful external lubricants (Behenyl-behenate) for PVC hard.

#### **Fatty alcohol esters of dicarboxylic acids**

10 These lubricants have, to a large extension, succeeded the free fatty alcohols. In particular because of their substantially lower volatility, they are superior to the basic materials. In its neutral behaviour, the fatty alcohol esters have much similarity to the wax esters, they are, however, significantly more compatible than those and can be used, for example, in the case of phthalic acid ester up to 5 phr 15 without clouding of the end product. Dicarboxylic acid esters are compatible with all stabiliser systems and are also suitable for the production of weather-resistant products. Because of the favourable compatibility-effectiveness ratio, they belong today to the most used lubricants.

20 **Amid waxes**

These high-melting products are often used as lubricant in the plastic industry. In addition to the simple fatty acid amids, stearic acid diamide of ethylenediamines (EDS) is used as separation and slipping agent in different thermoplasts; in the 25 USA the application of EDS in PVC processing is also wide spread. In Europe, on the other hand, EDS practically only finds use as antiblocking agent in soft and hard calander films. Since amid waxes reduce considerable the stability of PVC pieces, there are limits to an extended use from this point of view.

### **Metal soaps**

Among the metal soaps are found both relatively poor lubricants (calcium stearates) as well as products with strong external effects (zinc stearate, cadmium stearate, neutral lead stearate). Since all these soaps carry identical anionic groups, the different effects must be due to the cation, thus from different to polarity. As a common feature, the excellent separation effect of all metal soaps should be emphasised. The use as lubricants is limited by the pigment properties. A long way below the compatibility limits, most metal soaps already cloud PVC at relatively low doses. As a further disadvantage, an often undesired sweating out of soaps can be seen during PVC processing; despite this, metal soaps belong to the most important and most used PVC additives. They show good stabiliser properties and are used in lead systems as co-stabilisers, in barium-cadmium and calcium-zinc systems as primary stabilisers. Particularly good results are achieved in combination with epoxy plasticisers and lubricants with free hydroxyl groups.

### **Montan waxes**

The montanic acids and their derivatives belong to the oldest and most versatile PVC lubricants [3]. The crude wax is obtained from brown coal and transformed by oxidative bleaching into the long chain montanic acids. From this, ester waxes or soap-comprising waxes with complicated structures are obtained by esterification with diols or saponification with calcium hydroxide. These products are counted among the most effected separating agents; they still have an often astonishing compatibility. Thus, certain emulsion PVC types can absorb up to 6 parts of montan wax, and the partially saponified esters belong to the few solid lubricants which in PVC soft are well compatible. The main fields of application are calander processors, extrusion blow moulding and injection moulding. Because of

the complex production, montan waxes belong to the most expensive lubricants, so that some large fields of operation (pipe, profiles) remain closed to them.

### **Hydrocarbon waxes**

5

The hydrocarbons used technically as lubricants extend from paraffin oil to hard paraffin and to the polyethylene waxes. Both natural paraffins – obtained from petroleum residues and other native sources – and also pure synthetic products such as the Fischer-Tropsch-paraffines and PE-waxes are known. Apart from the 10 relatively well compatible highly branched liquid paraffin, the straight chain paraffines are outer lubricants, whose effectiveness increases with increasing chain length. All solid paraffines cause strong clouding in PVC even at low doses. The PE-waxes, both linear structured products if higher density as well as slightly branched products with lower density are among the most powerful outer lubricants. The former, the HDPE-waxes, have a relatively high clouding limit, which 15 does not correspond to their strong lubrication effect.

Paraffines and PE-waxes are used almost exclusively in extrusion processes, in particular in pipe manufacture. In particular, the application of weak stabilisers on 20 the basis of calcium stearate, as are common in France and in the USA, requires the use of larger amounts of hydrocarbon basis lubricants. By means of their strong external lubrication, the PVC is protected from friction heat. At the same time, these are processes which occur at relatively low material temperatures. The good “particle flow” which is absolutely necessary in these cases is enabled by the 25 addition of larger amounts of external lubricants (metal soaps, paraffines, PE-waxes).

Hydrocarbon waxes are however, used with lead stabilisers in pipe and profile manufacture; furthermore, PE-waxes are found with tin stabilisers in extruded

hard films and in flat formulations. Polyethylene waxes are also found in the production of PVC bottles. Here, their small influence on the transparency is exploited.

5 Shorter chain, branched, liquid paraffines are occasional components of soft PVC formulations. In particular with extrusion processes, use is also made here of hydrocarbons [25, 26].

### **Oxidised hydrocarbons**

10

By means of oxidation, polar groups, e.g. carboxyl, keto, hydroxy and ester functions, can be introduced into paraffines and PE-waxes. The compatibility and separation effect is significantly increased in this way. By saponification of the acidic groups, the polarity can be increased even further. These products, which 15 generally have very non-uniform structures, are, above all, effective with stabilisers such as tin carboxylates: They significantly reduce the strong wall adhesion of the PVC mixtures stabilised therewith and enable the formation of smooth profile surfaces.

20 **Lubricant mixtures**

For certain processing processes, the use of several lubricants is necessary [27 to 29]. These are principally extrusion processes, e.g. the production of types, profiles, plates, hollow bodies and injection mould articles. In order to safe the PVC 25 processor a problem of rheological adjustment and selection of lubricants, the additive manufactures offer lubricant combinations which comprises inner and outer lubricants in suitable adjustment and dosage [7]. A further rationalisation step is achieved by the use of stabiliser-lubricant compounds [30].

## **Lubricants in plasticiser-containing PVC pieces**

PVC soft is regarded as an easily processable material, yet even here there are many examples in which lubricants are used. To improve the rheology in fast occurring processes, to reduce friction and to extend path in the processing of injection moulding masses, to optimise the surface quality of the products, lubricants are used. Also, for improvement of tack-free properties and to achieve slip and antiblock effects, corresponding additives are necessary. They have already been reports in the description of use of different lubricants for a range of application examples; however, a few general applications rules should be added. With increasing plasticiser content, the compatibility of lubricants decreases, i.e. the risk of sweating out phenomena is significantly greater for PVC soft than in hard pieces. In principle – if selection is possible – liquid additives should be used. In the case of ester-type lubricants, unsaturated or branched compounds should be preferred. Almost all solid ester waxes are incompatible. The following solid lubricants can be used: Free fatty acids, such as stearic acid and 12-hydroxystearic acid, montanic acid ester and their partially saponified derivatives as well as amid wax of the type EDS. The compatibility of lubricants in the finished products should in every case also be investigated in long-term tests. Generally, liquid fatty acid esters of polyoles, such as glyceryl monoooleate, propylene glycol monoooleate, long chain unsaturated esters of phthalic acid as well as fatty acid esters of branched alcohols are regarded as well compatible. Unsaturated liquid fatty acid complex esters are also generally well compatible and, in limited dosages also solid products such as hardened caster oil and distearyl phthalate. On the other hand, caution should be exercised when using liquid glyceryl monoricinoleates; in the exclusive use of polymer plasticisers, practically every lubricant use must be selectively tested for compatibility.

### 6.5.5 Secondary effects of lubricants, influence on the physical-chemical value picture of PVC hard

When composing a PVC mixture for a particular processing process, the choice and dose of the lubricant are first made according to rheological and commercial considerations. It is required that a PVC semi-finished product can be produced commercially in continues operation in good quality. When adjusting the lubricant system, attention must further be paid to compatibility with the specified resin type, with the stabilisers and modification agents. Lubricant selection can, however, not only take into account the process conduct, but must also taken into account to the direct and indirect influence on the properties of the finished product. While under-lubrication would be immediately noticed during processing (material overheating, to high power input of the machines), over-lubricated material can be "smooth" to process. Over-lubrification leads, however, to insufficient material information and to the formation of thermal inhomogeneities and thus to impairment of the mechanical properties of the end product [31 to 33].

Lubricants have an influence on the transparency of films, plates and bottles. This must be taken into account in the formulation just as must as possible physiological aspects [21]. In the production of PVC packaging, care should be taken that the lubrication system does not impair smell and taste of the fill goods. Post-processing operations on films, such as deep-drawing, printing, adhering, welding, application of primers, must also be taken into account in the selection of the lubricant. Neither volatile lubricants nor larger quantities of incompatible lubricants may be used here. A number of the problems listed can be circumvented, if one uses lubricants which are as compatible as possible, in order to avoid critical doses of externally effective product. Internal lubricants have, however, some disadvantageous: They must be used in relatively high doses if sufficient lubrication effect is to be achieved; this leads to a more expensive formulation. In addition, well compatible lubricants have a softening influence, i.e. they decrease the

heat forming stability of PVC. Table 6.17 gives some relationships between type of the lubricant, dose and the depression of the Vicat softening temperature.

The aggregate state of the lubricant at room temperature has no measurable influence on the softening point PVC hard. Some lubricants, which are liquid at the softening point also have only little influence at practical doses on the heat formation stability. However, these are, without exception, products which do not belong to the range of internal lubricants. The influences amid waxes, montan waxes and fatty acid complex esters on the Vicat value can be ignored at usual dosage levels.

Table 6.17. Influences differently lubricants on the softening temperature of PVC hard (lead stabilisation)

Lubricant	Aggregate state	Vicat value <sup>1)</sup> (in °C) at		
		0.0 phr	0.5 phr	1.5 phr
Without lubricant	-	92	-	-
Distearyl phthalate	solid	-	91.5	88
Cetyl/stearyl alcohol	solid	-	90.5	88.5
Glyceryl monooleate	liquid	-	90.0	86.5
Glyceryl monoricinoleate	liquid	-	90.5	87.0
Glyceryl monostearate	solid	-	90.5	88.0
Glyceryl tri-12-hydroxystearate	solid	-	90.5	88.5
i-tridecyl stearate	liquid	-	89.5	86.5
Cetyl palmitate	solid	-	89.5	86.5
Stearyl stearate	solid	-	90.0	88
Cetyl/stearyl behenate	solid	-	90.5	89.5
Stearic acid	solid	-	92	92
12-Hydroxystearic acid	solid	-	91.5	91.5
Synthetic paraffin (SP: 105 °C)	solid	-	91.5	91.5

<sup>1)</sup>According to VDE 0302, measured in air.

According to this compilation of only the most important criteria, it is clear that it is certainly only possible in a few cases to make the lubricant selection of a formulation without compromise.

- 5 Apart from the special effect described in section 6.5.4, which are effected by partial esters of polyols and amid waxes [34], almost all lubricants make a positive contribution to long terms stability. By a limitation of friction and by material protection during the preparation and processing of PVC, an improvement of the reserve stability is achieved, which normally also expresses itself in an increased
- 10 light and/or weathering stability. As yet there are not findings for individual lubricant classes because of special investigations. Practical experience has shown, however, that above all ester waxes, dicarboxylic acid esters, but also metal soaps have proven themselves in many years of outdoor use [35, 36].
- 15 The influence of lubricants on mechanical properties of PVC hard products can be significant, if externally effective substances are used into high doses. These are, however, secondary effects, which occur as a result of "over-lubrication". Through insufficient plastification or inhomogeneous melting, in such cases optimal material properties cannot be achieved. Even at correct dosage, lubricants
- 20 have, a measurable influence on mechanical values, which is, however, difficult to test in practical applications (apart from softening point and cloud limit). In laboratory investigations, e.g. on press plates, lubricant influences on tensile strength, elasticity model and flexible impact resistance can be definitely demonstrated. These influences are relatively small. As would be expected, the influence of
- 25 outer lubricants is more pronounced. Often, in concentration-depend measurements, lubricant specific curves for the values mentioned appear, in which characteristic maxima and minima appear [33].

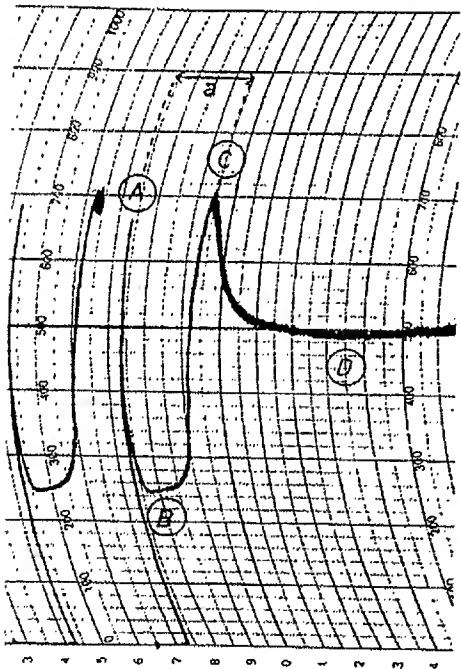
### 6.5.6 Lubricant tests

Tests on lubricants can be divided into two categories: One the one hand into material measurements on the substances themselves, on the other hand into measurements on PVC mixtures, in order to determine the difference influences of incorporated lubricants. In addition, the determination of additives in mixtures, granulates and finished products can also be of significance [37]. Physical and chemical material data are determined by manufacturers and processes of lubricants, in order to investigate identity and matching unity of the substances. Such determinations are relatively easy to carry out. They principally concern the determination of fat chemical data according to "German standard methods" [38], in addition, in some cases further physical measurements can be necessary [39].

Measurements carried out on PVC mixtures in order to check the influence of a lubricant or lubricant mixture on rheology, transparency, adhesion to the steel, stability and other properties. They serve either for research to the lubricant or formulation development. All rheological measurements are difficult. They are carried out on test apparatus which should simulate the behaviour of large processing machines, and, furthermore, the work should be done with small amounts of substance. The results obtained do not represent an absolute value. They are always comparative measurements referenced to a standard. This can be a known lubricant or a PVC mixture whose rheological behaviour should be set or readjusted. Final optimisation work is mostly carried out on production machines.



Picture 6.35. Opened kneader of a plastograph (Plasticorder PLV 151, Manufacturer: Brabender)



5 Picture 6.36. Plastogramm (double determination of the plastification time)

- A: End of the filling process, start of the powder lubrication
- B: Start of the powder friction,
- C: End of the first plastification period,
- D: Minimum torque of the PVC melt,

5 a: plastification time

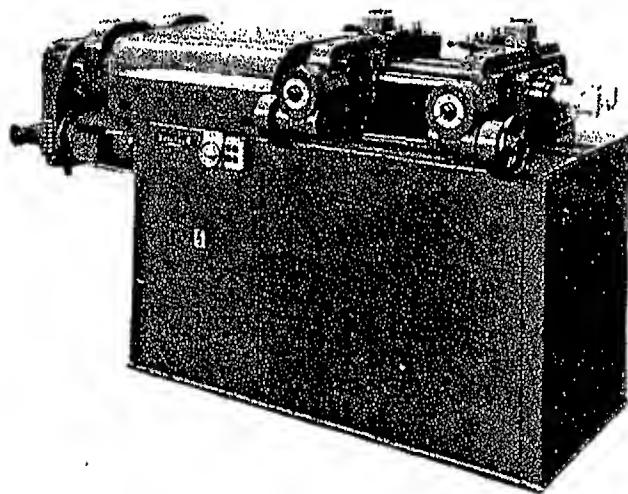
#### **6.5.6.1 Measurements with the plastograph**

Investigations with laboratories scale two shaft kneaders belong to the most common tests, if the effect of lubricants in PVC mixtures should be tested [40 to 47] (Picture 6.35). In a thermal stabilised kneading chamber, PVC dry mixtures are plasticised at constant rotation frequency of the kneader shovel. The resulting torque is measured over the entire course of the experiment and recorded graphically. Parallel thereto, the course of the temperature in the chamber is also measured. In these so-called plastograms, some important measurement parameters can be directly read and some others derived [48 to 50] (Picture 6.36). Particularly the influence of the lubricants on the plastification time is regarded by many authors as a measure of their compatibility and classification in the effect scale [15, 18]. Plastograph measurements are very exact within an array. In this way, lubricants with different chain length can be exactly distinguished definitely with a difference of two C-atoms, e.g. cetylstearate (total chain length: 34 C-atoms) compared to stearylstearate (36 C-atoms). For this reason, laboratory kneaders can also be used for the initial check of stabiliser/lubricant compounds. It is an advantage here that not only the rheological behaviour can be determined in the curve, but also very well the dynamic stability of the mixture.

#### **6.5.6.2 Measurements with the laboratory roller mill**

The mixing roller mill is equipped with two heatable rollers, whose rotation frequency and temperature can be adjusted independently of each other, and whose

separation is variable (Picture 6.37). It serves as aggregate for the production of homogenous PVC films, so-called rolling sheets, which are then needed for a range of tests, e.g. for determination of the transparency, the static stability, of blocking and slip behaviour and for compatibility investigations. Furthermore, the 5 roller mill also serves itself as a measurement instrument, e.g. for determination of the dynamic stability and for testing lubricants with respect to their separation activity. The time from providing the material up to adhesion of the skin on the roller is here decisive. Enormous differences partly arise for the individual lubricant classes [18]. Specially for the development of effective separating agents, 10 measurement with the laboratory roller mill cannot be replaced by any other.



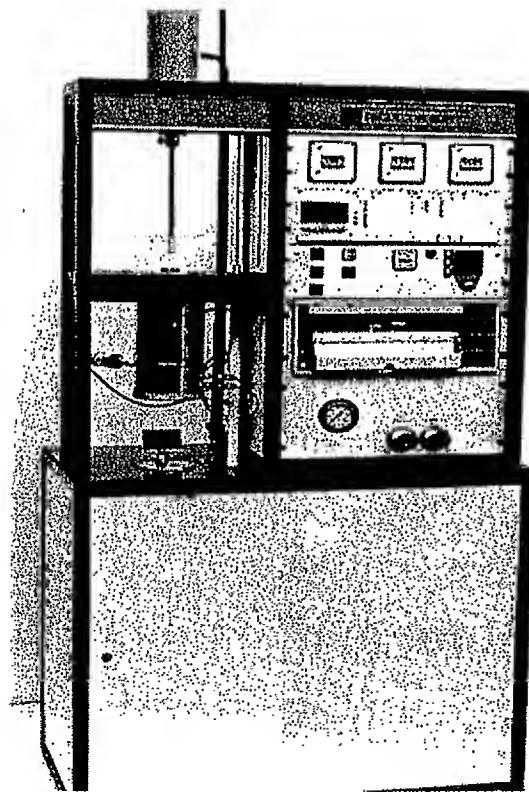
Picture 6.37 LABORWALZWERK (factory photo: Berstorff)

15 It is also possible to obtain approximate values for compatibility limits by determination of the plastification time, however, more exact values are obtained by measurements of the transparency and with the aid of plastograms. Roller mills, which are equipped with pressure sensors for determination of the disjoining pressure allow rheological work in advance for the adjustment of calander formulations (table 6.12).  
20

A further special measurement is the plate-out test. Here, with certain formulations, using a coating-giving and a coating-excepting rolling sheets, it can be established by means of simple colour measurement whether a PVC mixture tends 5 to sweating out of additives and pigments [39].

#### 6.5.6.3 Measurements with capillary viscosimeters

10 Capillary viscosimeters allow measurements of the flow behaviour of plasticised form masses. At constant temperature and pre-determined pressure or constant shear gradient, pre-plasticised material is pressed through a capillary, usually a standard nozzle. The output is measured independence on time (Picture 6.38).



Picture 6.38. Capillary rheometer (factory photo: Göttfert-Feinwerktechnik)

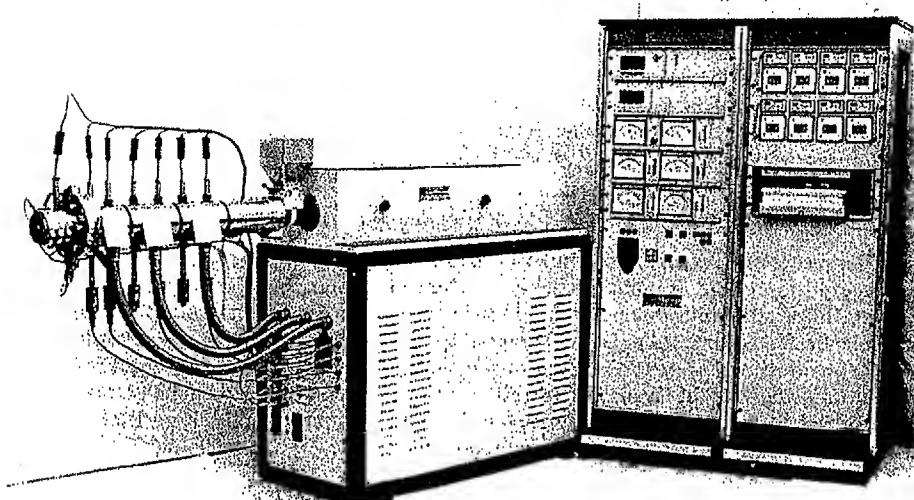
Lubricant test with viscosimeters are often carried out as purely research work, but also for series-wise checks of goods received with constant formulations [1 to 5 4, 51, 52]. The device is less suitable for the development of new form masses. On the one hand, the reproducibility of the results is difficult, on the other hand, despite the simple construction of the test device, quantitative conclusions can hardly be made. When carrying out comparative measurements, astonishingly good collaboration is achieved with plastograph results, if one concentrates very 10 rigorously on the behaviour of the lubricant in the melt [9].

#### **6.5.6.4 Lubricant investigations with the extrusiometer (measurement extruder)**

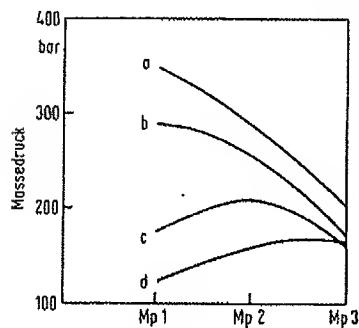
15 Laboratory extruders with screws of 20 to 30 mm diameter and a length of 15 to 25 D and good instrumentation are excellently suited for the investigation of lubricants. Temperature and rotation frequency can be varied within brought limits, in addition, screws with varying sections and different nozzles are available. Material pressures can be measured at several positions of cylinder and nozzle, discharge, torque and screws back pressure [3, 39, 53 to 56, 26] (Picture 6.39). The 20 extrusiometer does not only deliver data which can also be obtained in certain ranges in the capillary viscosimeter, but also a whole number of additional results. Practical information can be obtained regarding the influence of the lubricants on the gelling rate and valuable information for the application concerning the efficiency of the lubrication. Picture 6.40 shows the influence of various ester lubricants on the pressure course in the extruder (Picture 6.41). Comparison with plastograph findings show that this experimental results correspond excellently with 25 extrusiometer data. Plate out problems, in particular those which arise in extrusion processes, can likewise be investigated with a laboratory extruder without using

too much material. For such uses, special nozzles are proposed, in which a PVC mixture must rapidly flow through compression and expansion zones. The amount and composition of the coatings produced are temperature dependent, but above all formulation dependent [57].

5



Picture 6.39. Extrusionmeter (factory photo: Göttfert-Feinwerktechnik)

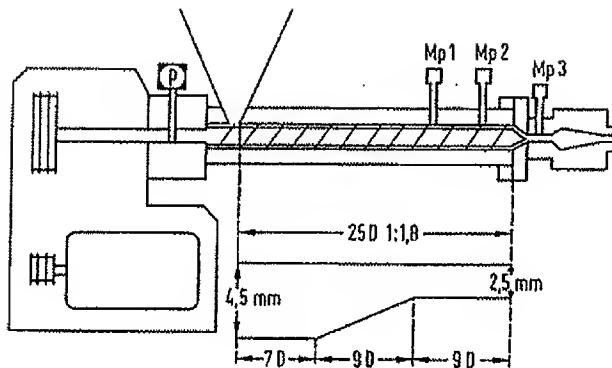


10

Picture 6.40. Pressure course of Pb-stabilised extrusion masses on addition of 1 phr of different ester lubricants; the pressure measurement positions marked with MP corresponds to those in picture 6.41

15 a: without lubricant  
b: distearyl phthalate

c: Lauryl stearate  
d: stearyl behenate



5

Picture 6.41. Schematic of an extrusiometer with three pressure measurement positions

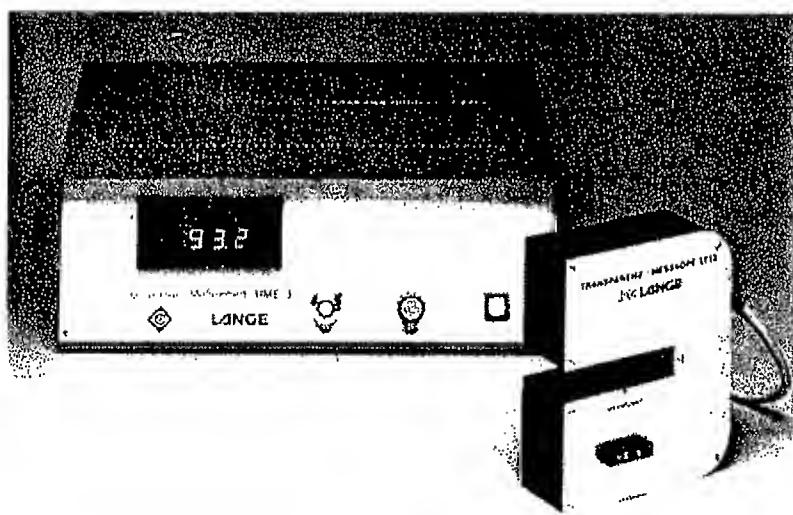
Further information possibilities arise from measurements of diverse extrusion data (swelling, colour, transparency, reserve stability, mechanical values and 10 weathering results). At least for extrusion processes, experiments with the extrusiometer do not only deliver valuable results for the researcher, but, above all, also practical results for the formulation development.

#### 6.5.6.5 Transparency measurements

15 Since lubricants influence the transparency of PVC articles, measurements are often carried out in order to determine their suitability for the production of glass-clear PVC products, such as films, plates, bottles and injection moulded articles. The adjustment and checking of such a formulation does not necessarily have to 20 occur under conditions common in practise. With the aid of measurements on press plates, precise information regarding the influence of the formulation partners on the transparency can be obtained. Such investigations have shown that there are close relationships between the compatibility of lubricants and the influ-

ences on clarity of PVC plates. These relationships hold at least for lubricants with polar groups.

For this reason, transparency measurements are also used in research work; the 5 experimental determination of clouding limits in most cases provides usable information concerning the activity limits of a lubricant, i.e. regarding the transition from internal to external lubrication [2, 15, 118, 58]. Press plates are generally prepared from rolling sheets. By using suitable press forms and covering with chromed plates or films, one obtains plates with a defined thickness and smooth 10 surface. Normally, measurements are carried out on 2 to 4 mm thick plates. Alkyltinthioglycolates are used as stabilisers, i.e. highly effective products which have practically no influence on the transparency. The lubricants are advantageously dosed in stepped amounts, with highly compatible substances in steps of 1.0 phr, with externally effective products in intervals of 0.1 phr. The measurements 15 are carried out using a transparency measuring device, whereby only clouding occurrences are determined. Colour influences are corrected by means of filters (Picture 6.42.)

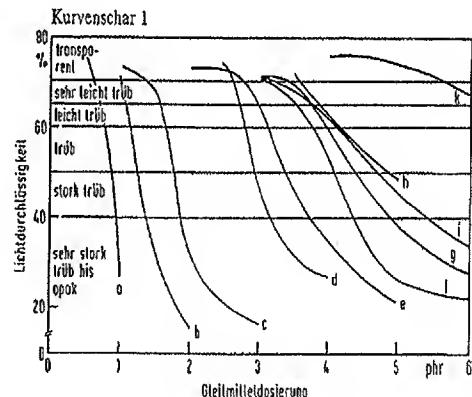


20 Picture 6.42. Transparency measurements device (factory photo Dr. Lange)

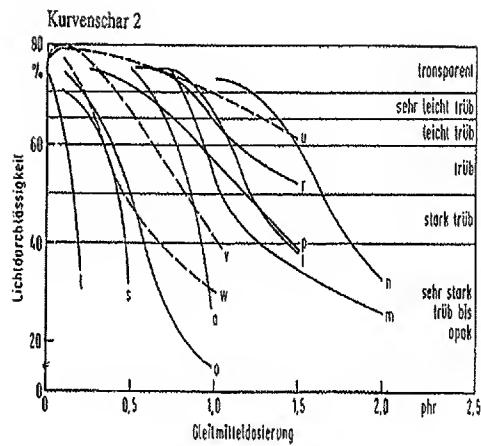
Opacity and/or transparency measurements can also be carried out with a colour measurement heat. The sets of curves 1 and 2 were obtained by this method. They show that the clouding limits of well compatible internal lubricants lie around 3 to 5 phr; the clouding does not occur abruptly but gradually. Strong external lubricants show a steep dropping of at extremely low limiting dosage, while the bulk of the common waxes shows limits between 0.5 and 1.0 phr, but drops of relatively steeply. Fatty acids here achieve remarkably high clouding limits with flat gradients – compared with their effectiveness measured on rheological instruments. The separating agents, such as higher molecular esters and montan waxes, also show such a flat transparency fall at increasing dosage; amid waxes show a similar curve (Picture 6.43, 6.44).

15 For picture 6.43

- a: stearyl behenate
- b: stearyl stearate
- c: cetyl palmitate
- d: i-tridecyl stearate
- 20 e: glyceryl monostearate
- f: hardened castor oil
- g: glyceryl monooleate
- h: stearyl alcohol
- i: glyceryl monoricinoleate
- 25 k: distearyl phthalate



- a: stearyl behenate
- l: Fischer-Tropsch-Paraffin
- 5 m: palmitic/stearic acid
- n: 12-hydroxystearic acid
- o: montan acid ester
- p: high molecular fatty acid ester
- r: ethylenediamine distearate
- 10 s: paraffin
- t: paraffin oil
- u: oxidised PE wax
- v: oxidised PE wax
- w: PE wax



Picture 6.43 and 6.44. clouding limits when using different lubricants in dependence on the dose;

20 100 weight parts S-PVC, K-value 60, 1.5 weight parts tin stabiliser; measurement according to DIN 53147 in 4 mm press plates, without lubricant a transparency of 74 % is found.

#### 6.5.6.6 Spiral test

25 This test is carried out using a spiral form at injection moulding machines. By injecting into the spiral form and measurement of the flow path, the flowability of a mass can be determined. In principle, rheological measurements on injection moulding masses can also be carried out on laboratory scale with the high pressure capillary viscosimeter, with significantly lower test complexity. The spiral test is, however, more practical: The actual flow path dependent on form temperature, mass temperature and type of sprue can be better tested with the spiral form.

30 In addition, the surface formation of the injection-moulded part can be observed dependent on the wall adhesion. The influence of the formulation partners, particularly of the lubricants, can thus be evaluated in approximation to operating

conditions. It is a disadvantage that further typical injection problems, such as flow line welding and air inclusions (mould venting) cannot be studied with the spiral form [59].

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